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(54) EXHAUST GAS PURIFYING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve durability compared with the conventional catalyst and to exhibit excellent low temp. activity and purification efficiency, particularly excellent HC purification efficiency particularly after high temp. endurance at the time of purifying a low temp. exhaust gas.

SOLUTION: At the time of purifying the low temp. exhaust gas, a catalyst containing an oxygen adsorbent having oxygen storing ability selectively separating and adsorbing oxygen from the exhaust gas at a temp ranging from room temp. to 200°C and having oxygen releasing ability at a temp. ranging from 200-400°C is arranged at the upstream side to the exhaust gas flow, a catalyst containing a hydrocarbon adsorbent having hydrocarbon adsorbing ability at a temp. ranging from room temp. to 150°C and having hydrocarbon releasing and purifying ability at 150°C and a noble metal is arranged at the downstream side, a valve capable of switching an exhaust gas flow passage is arranged at the more upstream side of the catalyst arranged at the upstream side, the arrangement of the catalysts are set so as to supply oxygen through the upstream side catalyst to the downstream side catalyst when the catalyst arranged at the downstream side releases and purifies hydrocarbon at a catalytic temp. of 150-300°C and the valve is controlled corresponding to the temp. of the catalytic layer of the upstream side catalyst.

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CLAIMS

[Claim(s)]

[Claim 1] In purifying low-temperature exhaust gas, exhaust gas flow is received. To the upstream The catalyst for which catalyst bed temperature contains the oxygen adsorption material which has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in a 200-degree C temperature region, and has oxygen emission ability in a 200 degrees C - 400 degrees C temperature region is arranged. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C It is the exhaust gas purification approach which the above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and is characterized by adjusting said bulb according to the temperature in the catalyst bed of the catalyst of the upstream.

[Claim 2] The catalyst arranged to the upstream is SiO₂ / aluminum 2O₃ as oxygen adsorption material. The exhaust gas purification approach according to claim 1 characterized by a ratio containing 20 or less A mold and X zeolite.

[Claim 3] The exhaust gas purification approach according to claim 1 or 2 characterized by preventing flowing into the catalyst to which the bulb installed in the upstream of this catalyst was operated, exhaust gas passage was changed, and exhaust gas has arranged the temperature of 400 degrees C or more to the upstream concerned when the temperature in the catalyst bed of the catalyst arranged to the upstream reaches 400 degrees C.

[Claim 4] The catalyst arranged to the upstream is the next empirical formula:[A] [B] Oy (it La(s) among a formula A). The element more than a kind chosen from the group which consists of Sr, Ba, Pb, Nd, and Ce, The element more than a kind chosen from the group which B becomes from aluminum, Ti, Cr, Mn, Co, Fe, and nickel, an oxygen atomic number required for O to show oxygen and for y satisfy the valence of each element -- being shown -- claims 1-3 characterized by containing the multiple oxide of the perovskite type structure expressed -- the exhaust gas purification approach given [one of] in a term.

[Claim 5] The catalyst arranged to the upstream is the exhaust gas purification approach according to claim 1 to 4 characterized by containing the cerium oxide which supported platinum and/or palladium.

[Claim 6] The catalyst arranged to the downstream is the exhaust gas purification approach according to claim 1 to 5 characterized by containing the zeolite more than a kind chosen from the group which consists of ZSM5, USY, and a beta-zeolite as hydrocarbon adsorption material, the metal more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound.

[Claim 7] Hydrocarbon adsorption material is the exhaust gas purification approach according to claim 6 characterized by containing the element more than a kind chosen from the group which consists of platinum, palladium, Linn, boron, magnesium, and calcium.

[Claim 8] the element more than a kind chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum -- metal conversion -- 1-40-mol % and a cerium -- 60-98-mol % -- the exhaust gas purification approach according to claim 6 or 7 characterized by arranging the catalyst component layer containing the included cerium oxide.

[Claim 9] The exhaust gas purification approach according to claim 8 further characterized by arranging the catalyst component layer containing the zirconic acid ghost which contains a 1-30 mol % zirconium for the element more than a kind chosen from the group which consists of platinum, a rhodium, a cerium, neodium, and a lanthanum 70 to 98% by metal conversion, and an activated alumina in the upper part of the catalyst component layer containing the palladium arranged in the upper part of a hydrocarbon adsorption material layer.

[Claim 10] The exhaust gas purification approach according to claim 8 or 9 characterized by arranging the three way component catalyst which was chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from alkali metal and alkaline earth metal, and which a kind contains at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the exhaust gas purification approach which can purify HC efficiently especially among the hydrocarbon in the exhaust gas discharged from internal combustion engines, such as an automobile, at the time of the low temperature immediately after engine starting ("HC" is called hereafter), a carbon monoxide ("CO" is called below), and a nitriding oxide ("NOx" is called hereafter) about the exhaust gas purification approach.

[0002]

[Description of the Prior Art] the approach of desorb, after use HC adsorption material, store temporarily for the purpose of reduction of the hydrocarbon in the exhaust gas discharge at the time of the low temperature immediately after engine starting ("cold HC" be call hereafter) and activate a three way component catalyst from before, since the catalyst for exhaust gas purification do not have the enough endurance under an elevated temperature, a catalyst deteriorate and decontamination capacity fall remarkably, and purify with this three way component catalyst be examine.

[0003] As a catalyst for exhaust gas purification using this HC adsorption material, there are some which are indicated by JP,6-74019,A, JP,7-144119,A, JP,6-142457,A, JP,5-59942,A, or JP,7-102957,A, for example.

[0004] After establishing bypass passage in exhaust air passage, making JP,6-74019,A once stick to HC adsorption material which has arranged HC discharged at the time of cold one immediately after engine starting to bypass passage, switching exhaust air passage to it after that and activating a down-stream three way component catalyst, the system which purifies gradually HC desorbed through HC adsorption catalyst from a part of exhaust gas with a latter three way component catalyst is proposed.

[0005] In JP,7-144119,A, heat is taken by the three way component catalyst of the preceding paragraph at the time of cold one immediately after engine starting, the adsorption effectiveness of HC adsorption material of the middle is raised, and the system which makes heat transfer of the heat of reaction easy to carry out to a latter three way component catalyst through HC adsorption material of the middle which carried out tandem arrangement in after three way component catalyst activation of the preceding paragraph, and promotes purification with a latter three way component catalyst is proposed.

[0006] In case HC to which it stuck in the low-temperature region ****s, the preheating of the exhaust gas including Desorption HC is carried out by the heat exchanger, and the cold HC adsorption treatment system which promotes purification with a three way component catalyst is proposed by JP,6-142457,A.

[0007] By switching the passage of the exhaust gas by catalyst arrangement and the bulb, the temperature up of HC adsorption material is made slow, and the system which improves the adsorption effectiveness of cold HC is proposed by JP,5-59942,A.

[0008] Moreover, in order to improve the purification engine performance of a latter oxidation and three way component catalyst, air is supplied between the three way component catalyst of the preceding paragraph, and HC adsorption material of the middle, and the system which promotes activation of a

latter oxidation and three way component catalyst is proposed by JP,7-102957,A.

[0009]

[Problem(s) to be Solved by the Invention] However, HC adsorption effectiveness falls after durability, moreover, since the conventional system using HC adsorption material indicated in said official report of the endurance of HC adsorption material is inadequate, before a latter three way component catalyst is activated, HC will **** and emission will be worsened in it.

[0010] Then, in order to attain improvement in adsorption effectiveness and the formation of desorption delay of HC adsorption material, the heat exchanger for the method of bypassing elevated-temperature gas or three way component catalyst pre-heating is used, but while a system configuration makes it complicated, sufficient effectiveness is not acquired, but since cost goes up remarkably, moreover, HC adsorption material with high endurance and adsorption effectiveness is desired.

[0011] In order to use noble metals so much in order to maintain the high purification engine performance from the first stage to until after durability, or to aim at promotion of purification of early activation and Desorption HC, especially the three way component catalyst aiming at purification of HC desorbed from HC adsorption material introduces air, and is shining and carrying out it. For this reason, although a catalyst from which the purification engine performance in which the amount of noble metals to be used is high at least is obtained was desired, when noble metals were reduced, endurance became inadequate and after durability had the problem that the catalytic activity and the purification engine performance in a low-temperature region got worse.

[0012] Therefore, in purifying low-temperature exhaust gas, the purpose of this invention is to offer the exhaust gas purification approach which shows the low-temperature activity and the purification engine performance which endurance improved and the conventional catalyst was excelled especially after elevated-temperature durability, and HC purification effectiveness in which it excelled especially.

[0013]

[Means for Solving the Problem] In purification of the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as a result of inquiring, in order that this invention persons may solve the above-mentioned technical problem The catalyst which has hydrocarbon adsorption and decontamination capacity for the catalyst which has oxygen storage / emission ability in the upstream of exhaust gas in the downstream is arranged. When the catalyst of the downstream ****ed and purified a hydrocarbon, HC purification effectiveness at the time of cold HC to which it stuck ****ing reached [being improved and maintained remarkably and] a header and this invention by supplying oxygen to the catalyst of the downstream from the catalyst of the upstream.

[0014] In the exhaust gas purification approach according to claim 1 purifying low-temperature exhaust gas The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and it is characterized by adjusting said bulb according to the temperature in the catalyst bed of the catalyst of the upstream.

[0015] For the exhaust gas purification approach according to claim 2, the catalyst arranged to the upstream in the exhaust gas purification approach according to claim 1 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. It is characterized by a ratio containing 20 or less A mold and X zeolite.

[0016] The exhaust gas purification approach according to claim 3 is characterized by preventing flowing into the catalyst to which the bulb installed in the upstream of this catalyst was operated,

exhaust gas passage was changed, and exhaust gas has arranged the temperature of 400 degrees C or more to the upstream concerned, when the temperature in the catalyst bed of the catalyst arranged to the upstream reaches 400 degrees C in the exhaust gas purification approach according to claim 1 or 2.

[0017] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 4 -- claims 1-3 -- the catalyst arranged to the upstream -- the next empirical formula:[A] [B] Oy (the element more than a kind chosen from the group which A becomes from La, Sr, Ba, Pb, Nd, and Ce among a formula, and B) an oxygen atomic number required for the element more than a kind chosen from the group which consists of aluminum, Ti, Cr, Mn, Co, Fe, and nickel, and O to show oxygen, and for y satisfy the valence of each element -- being shown -- it is characterized by containing the multiple oxide of the perovskite type structure expressed.

[0018] the exhaust gas purification approach according to claim 5 -- claims 1-4 -- in the exhaust gas purification approach given [one of] in a term, the catalyst arranged to the upstream is characterized by containing the cerium oxide which supported platinum and/or palladium.

[0019] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 6 -- claims 1-5 -- The zeolite more than a kind chosen from the group which the catalyst arranged to the downstream becomes from ZSM5, USY, and beta-zeolite as hydrocarbon adsorption material, It is characterized by containing the metal more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound.

[0020] The exhaust gas purification approach according to claim 7 is characterized by hydrocarbon adsorption material containing the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium in the exhaust gas purification approach according to claim 6.

[0021] the element more than a kind chosen from the group to which the exhaust gas purification approach according to claim 8 becomes the upper part of a hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in the exhaust gas purification approach according to claim 7 -- metal conversion -- 1-40-mol % and a cerium -- 60-98-mol % -- it is characterized by arranging the catalyst component layer containing the included cerium oxide.

[0022] The exhaust gas purification approach according to claim 9 is set to the exhaust gas purification approach according to claim 8. In the upper part of the catalyst component layer containing the palladium arranged in the upper part of a hydrocarbon adsorption material layer Furthermore, the zirconic acid ghost which contains a 1-30 mol % zirconium for a kind chosen from the group which consists of platinum, a rhodium, a cerium, neodium, and a lanthanum 70 to 98% by metal conversion, The exhaust gas purification approach according to claim 8 characterized by arranging the catalyst component layer containing an activated alumina.

[0023] The exhaust gas purification approach according to claim 10 is characterized by arranging the three way component catalyst which was chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from alkali metal and alkaline earth metal and which a kind contains at least in the exhaust gas purification approach according to claim 8 or 9.

[0024]

[Embodiment of the Invention] In purifying the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as the exhaust gas purification approach of this invention The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream

****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and said bulb can improve the desorption hydrocarbon purification effectiveness of the catalyst of this downstream by considering as the configuration adjusted according to the temperature in the catalyst bed of the catalyst of the upstream.

[0025] The oxygen adsorption material ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains is SiO₂ / aluminum 2O₃ which can dissociate and adsorb oxygen alternatively out of low-temperature exhaust gas. 20 or less A mold and an X type zeolite have an effective ratio. Catalyst bed temperature separates and stores the oxygen in exhaust gas alternatively from a room temperature in a 200-degree C temperature region, and can emit oxygen in a 200 to 400 degrees C temperature region, the catalyst which made this zeolite contain can supply oxygen efficiently, in case the catalyst of the downstream ****s and purifies the hydrocarbon to which it stuck from low-temperature exhaust gas, and it can raise HC purification effectiveness of noble metals. As for the amount, per [catalyst 1L / 10g-300g] are desirable from the point of the improvement in the engine performance.

[0026] Moreover, although the bulb installed in the upstream of this catalyst is operated and exhaust gas passage is changed when the temperature in the catalyst bed of this upstream (a thermometric element is installed into the catalyst bed concerned, and temperature is detected) reaches 400 degrees C, this is for preventing that exhaust gas with a temperature of 400 degrees C or more flows into oxygen adsorption material, and preventing the structure destruction by the heat of this zeolite.

[0027] moreover -- as the ingredient which was excellent in thermal resistance in order that the catalyst arranged to this upstream might emit oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more -- the next empirical formula:[A] [B] Oy (A) The element more than a kind chosen from the group which consists of La, Sr, Ba, Pb, Nd, and Ce, and B an oxygen atomic number required for the element more than a kind chosen from the group which consists of Al, Ti, Cr, Mn, Co, Fe, and Ni, and O to show oxygen, and for y satisfy the valence of each element -- being shown -- the multiple oxide of the oxygen migratory high perovskite type structure expressed can be contained. By this, the degradation of the oxygen adsorption material slack zeolite arranged to this upstream can be compensated, and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved further.

[0028] Furthermore, since the catalyst arranged to this upstream promotes the operation which emits oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more, the cerium oxide which supported platinum and/or palladium can be made to contain. By making this catalyst contain platinum and/or a palladium support cerium oxide, the endurance of the catalyst arranged to the upstream improves and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved over a long period of time.

[0029] As amount of the sum total used of the ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains, they are the above, and SiO₂ / aluminum 2O₃. Per [upper catalyst 1L / 10g-300g] are desirable combining the cerium oxide with which the ratio supported 20 or less A mold and an X type zeolite, the multiple oxide of perovskite type structure, and platinum and/or palladium. The adsorption engine performance is saturated with less than 10g, and the amount of the ingredient used which has oxygen storage / supply ability is not economically effective at it, even if the adsorption engine performance is not fully discovered and exceeds 300g conversely.

[0030] Moreover, as an ingredient which adsorbs the hydrocarbon discharged in the low-temperature region arranged at the downstream, they are SiO₂ / aluminum 2O₃. The various hydrocarbons discharged in a low-temperature region can be efficiently adsorbed by using more than a kind chosen from the group which a ratio becomes from 20 or more ZSM5, USY(s), and beta-zeolites. As for the amount of the hydrocarbon adsorption material used, per [catalyst 1L / 10g-300g] are desirable. The adsorption engine performance is saturated with less than 10g, and the amount of the hydrocarbon adsorption material used is not economically effective at it, even if the adsorption engine performance is

not fully discovered and exceeds 300g conversely. Furthermore, since the hydrocarbon desorbed from this hydrocarbon adsorption material is purified, the hydrocarbon from which it is desorbed with the rise of catalyst bed temperature can be efficiently purified by containing the element more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound. 1g-30g, and an activated alumina are [10g-300g, and Seria oxide / 5g-100g, and a zirconic acid ghost / 5g-100g, and a barium compound] desirable [the amount / per / catalyst 1L / and noble metals / that they are 1g-50g] from the point which purifies Desorption HC efficiently.

[0031] Furthermore, since the structural stability under the elevated temperature of hydrocarbon adsorption material (thermal resistance), adsorption capacity cold [HC], and HC desorption control engine performance at the time of a temperature rise are improved, the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium can be contained. The content of this element is 10 % of the weight from 0.1 % of the weight to HC adsorption material. If it is less than 0.1 % of the weight, sufficient amelioration effectiveness will not be acquired, but if it is conversely used mostly from 10 % of the weight, the pore of a zeolite will blockade and HC adsorption capacity will fall.

[0032] furthermore, the element more than a kind chosen from the group which becomes the upper part of this hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in order to improve the purification effectiveness at the time of HC to which it stuck by hydrocarbon adsorption material ****ing -- metal conversion -- a 1-40 mol % cerium -- 60-98-mol % -- the catalyst component layer containing the included cerium oxide can be arranged. In order to raise the purification engine performance and endurance of palladium especially, in a palladium content catalyst component layer the element more than a kind chosen from the group which consists of a zirconium, neodium, and a lanthanum -- metal conversion -- a 1-40 mol % cerium -- 60-98-mol % -- by making the included cerium oxide contain Since the high cerium oxide of oxygen occlusion ability becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidization condition of palladium, and the fall of the catalyst ability of palladium can be controlled. As for the amount of this palladium used, it is desirable from the point of the purification engine performance that they are per [catalyst 1L / 1g-30g]. The amount of this cerium oxide used is per [catalyst 1L / 5-100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0033] furthermore, the element more than a kind chosen from the group which becomes the upper part of the catalyst component layer containing palladium from platinum, a rhodium, a cerium, neodium, and a lanthanum in order to improve the poisoning-proof nature and the purification engine performance of palladium -- metal conversion -- a 1-30 mol % zirconium -- 70-98-mol % -- the catalyst component layer containing the included zirconic acid ghost and an activated alumina can be arranged. As a base material with which said platinum and rhodium are supported, in order to raise the endurance of platinum or a rhodium, a zirconic acid ghost is suitable. Since the high cerium content zirconic acid ghost of oxygen occlusion ability especially becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidization condition of platinum or a rhodium, and the fall of the catalyst ability of platinum or a rhodium can be controlled.

[0034] The cerium content of this zirconic acid ghost is 0.01-mol % to 30-mol %. Less than [0.01 mol %], a cerium content is ZrO_2 . ZrO_2 of the element which was not different from a case and was described above If the amelioration effectiveness by the oxygen occlusion ability of a cerium does not show up and a cerium content exceeds 30-mol %, a BET specific surface area and thermal stability will fall [this effectiveness] to saturation or reverse. The amount of the zirconic acid ghost used is per [catalyst 1L / 5-100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0035] Moreover, since the low-temperature activity of palladium is improved, the three way component catalyst containing alkali metal and/or alkaline earth metal can be arranged. There are a potassium, calcium, strontium, barium, sodium, magnesium, an yttrium, a lanthanum, etc. in these metals. The content of this element is among [1-40g] catalyst 1L. In less than 1g, neither relaxation of adsorption poisoning to the noble metals of HC nor sintering of palladium can be controlled, but even if it exceeds 40g, the capable increase-in-quantity effectiveness is not acquired, but the engine performance is reduced conversely.

[0036]

[Example] The example of preparation, a following example, and the following example of a comparison explain this invention. The section is weight ***** as long as there is especially no display.

[0037] A mold zeolite powder of example of preparation 1SiO₂/aluminum₂ O₃ =15 The 400 sections, Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy Perovskite mold multiple oxide powder The 250 sections, The palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1% of palladium support concentration The 250 sections, With the 500 sections, 2000g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst A of amount weight of coats 300 g/L-support was acquired. The amount of palladium support was 2.12g/cf (0.075 g/L).

[0038] The 200 sections and USY of SiO₂/aluminum₂ O₃ =25 for the 600 sections and ZSM5 of SiO₂/aluminum₂ O₃ =50 The 100 sections, [beta-zeolite powder of example of preparation 2SiO₂/aluminum₂ O₃ =25] With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst of amount weight of coats 200 g/L-support was acquired (catalyst B).

[0039] After sinking the palladium nitrate water solution into the alumina powder (powder A) containing cerium 3 mol % (it converts into CeO₂ and is 8.7 % of the weight), zirconium 3 mol % (it converts into ZrO₂ and is 6.3 % of the weight), and lanthanum 2 mol % (it converts into La₂O₃, and is 5.5 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support alumina powder (powder B) was obtained. Pd concentration of this powder B was 11 % of the weight.

[0040] After sinking the palladium nitrate water solution into the cerium oxide powder (powder C) containing lanthanum 1 mol % (it converts into La₂O₃, and is 2 % of the weight), and zirconium 32 mol % (it converts into ZrO₂ and is 25 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder (powder D) was obtained. Pd concentration of this powder D was 2.5 % of the weight.

[0041] The above-mentioned powder B880g, powder D280g, 40g of activated aluminas, and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst B, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 260g / L-support was acquired. The amount of palladium support was 146.67g/cf (5.18 g/L) (catalyst C).

[0042] Subsequently, after sinking a nitric-acid rhodium water solution into the activated-alumina object powder (powder E) which supported 3 % of the weight of Zr and drying at 150 degrees C for 12 hours, it calcinates at 400 degrees C for 1 hour, and it is 3 % of the weight-aluminum₂ O₃ of Rh support Zr. Powder (powder F) was obtained. Rh concentration of this powder F was 2.0 % of the weight.

[0043] The 300 sections, the activated-alumina 30 section, and 1500g of nitric-acid water solutions were

fed into the magnetic ball mill for the 470 sections and zirconic acid ghost powder (La1 mol %, Ce20 mol %, and Zr79 mol %) (powder F), the above-mentioned powder E was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst C, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 300g / L-support was acquired. The amount of rhodium support was 13.33 g/cf (0.47 g/L) (catalyst D).

[0044] E Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10 g/L was made to contain as BaO, and the down-stream catalyst was acquired.

[0045] In the A mold zeolite powder 400 section of example of preparation 3SiO₂/aluminum₂ O₃ =15, instead of, The X type zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 400 sections.

Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.5} Sr_{0.2} Ba_{0.2} Ce_{0.05}Nd_{0.05}] and [Cr_{0.1} Mn_{0.3} Fe_{0.1} nickel_{0.1} aluminum_{0.05}Ti_{0.05}] The perovskite mold multiple oxide powder of Oy is made into the 250 sections. Except having used the amount of the platinum support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of platinum support concentration as the 250 sections, the upper catalyst F was acquired according to the example 1.

[0046] In the A mold zeolite powder 400 section of example of preparation 4SiO₂/aluminum₂ O₃ =15, instead of, The 100 sections and the X type zeolite powder of SiO₂/aluminum₂O₃ =15 are made into the 100 sections for A mold zeolite powder of aluminum₂O₃/aluminum₂ O₃ =15. Empirical formula:

[La_{0.6} Sr_{0.3}Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.5} Sr_{0.2} Ba_{0.2} Ce_{0.05}Nd_{0.05}] and [Cr_{0.1} Mn_{0.3} Fe_{0.1} nickel_{0.1} aluminum_{0.05}Ti_{0.05}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 600 sections, the upper catalyst G was acquired according to the example 1.

[0047] In the A mold zeolite powder 400 section of example of preparation 5SiO₂/aluminum₂ O₃ =15, instead of, The 50 sections and the X type zeolite powder of SiO₂/aluminum₂ O₃=15 are made into the 50 sections for A mold zeolite powder of SiO₂/aluminum₂ O₃ =15. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 700 sections, the upper catalyst H was acquired according to the example 1.

[0048] In the A mold zeolite powder 400 section of example of preparation 6SiO₂/aluminum₂ O₃ =15, instead of, A mold zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 50 sections. Empirical formula: [La_{0.6}Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy It considers as the perovskite mold multiple oxide powder 50 section. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 900 sections, the upper catalyst H was acquired according to the example 1.

[0049] In the A mold zeolite powder 400 section of example of preparation 7SiO₂/aluminum₂ O₃ =15, instead of, The X type zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 50 sections. Empirical formula: [La_{0.6}Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, Empirical formula [La_{0.9} Sr_{0.1}] Oy Perovskite mold multiple oxide powder is made into the 50 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 800 sections, the upper catalyst J was acquired according to the example 1.

[0050] The beta-zeolite powder 600 section of example of preparation 8SiO₂/aluminum₂ O₃ =25, ZSM5 of SiO₂/aluminum₂ O₃ =50 In the 200 sections and the USY100 section of SiO₂/aluminum₂ O₃

=25, instead of, According to the example 2, the down-stream catalyst K was acquired except having used [the amount of beta-zeolite powder of SiO₂/aluminum₂ O₃ =25] the 50 sections and the amount of USY of SiO₂/aluminum₂ O₃ =25 for the 800 sections and the amount of ZSM5 of SiO₂/aluminum₂ O₃ =50 as the 50 sections.

[0051] In the beta-zeolite powder 600 section of example of preparation 9SiO₂/aluminum₂ O₃ =25, instead of, According to the example 2, the down-stream catalyst L was further acquired except not using ZSM5 of SiO₂/aluminum₂ O₃ =50, and USY of SiO₂/aluminum₂ O₃ =25, using the amount of beta-zeolite powder of SiO₂/aluminum₂ O₃ =25 as the 900 sections.

[0052] ZSM5 of example of preparation 10SiO₂/aluminum₂ O₃ =50 The 200 sections, The USY100 section of SiO₂/aluminum₂ O₃ =25 is replaced. ZSM5 of SiO₂/aluminum₂ O₃ =50 The 400 sections, According to the example 2, the down-stream catalyst M was acquired except not using beta-zeolite powder of SiO₂/aluminum₂ O₃ =25 further, using the amount of USY of SiO₂/aluminum₂ O₃ =25 as the 500 sections.

[0053] According to the example 9, the down-stream catalyst N was acquired except having used the beta-zeolite 900 section of SiO₂/aluminum₂ O₃ =50 containing 0.5 % of the weight of boron, and 0.1 % of the weight of calcium instead of the beta-zeolite powder 900 section of example of preparation 11SiO₂/aluminum₂ O₃ =50.

[0054] The beta-zeolite powder 600 section of example of preparation 12SiO₂/aluminum₂ O₃ =25, ZSM5 of SiO₂/aluminum₂ O₃ =50 In the 200 sections and the USY100 section of SiO₂/aluminum₂ O₃ =25, instead of, The beta-zeolite 700 section of SiO₂/aluminum₂ O₃ =25 containing 0.1 % of the weight of Linn, 0.1 % of the weight of magnesium, and 0.1 % of the weight of palladium, ZSM5 of SiO₂/aluminum₂ O₃ =50 containing 0.1 % of the weight of platinum, 0.1 % of the weight of boron, and 0.1 % of the weight of calcium The 100 sections, According to the example 9, the down-stream catalyst O was acquired except having used the USY100 section of SiO₂/aluminum₂ O₃ =25 containing 0.5 % of the weight of Linn, and 0.1 % of the weight of calcium.

[0055] According to the example 1, the upper catalyst P was acquired except having used only the A mold zeolite powder 900 section of example of comparison preparation 1SiO₂/aluminum₂ O₃ =15, and the silica sol (SiO₂ as concentration 20%) 500 section.

[0056] According to the example 1, the upper catalyst Q was acquired except having used only the example of comparison preparation 2[La_{0.6} Sr_{0.3} Ba_{0.1}] [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy powder 900 section, and the silica sol (SiO₂ as concentration 20%) 500 section.

[0057] According to the example 1, the upper catalyst R was acquired except having used only the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder 900 section of 0.1 % of the weight of example of comparison preparation 3 palladium support concentration, and the silica sol (SiO₂ as concentration 20%) 500 section.

[0058] Powder B880g and powder D280g which was obtained in the example of comparison preparation 4 example 2, and 40g of activated aluminas and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 60g / L-support was acquired. The amount of palladium support was 146.67g/cf (5.18 g/L) (catalyst S).

[0059] Subsequently, with the powder E470 section obtained in the example 2, the zirconic acid ghost powder (powder F) 300 section (La₁ mol %, Ce₂₀ mol %, and Zr₇₉ mol %), and the activated-alumina 30 section, 1500g of nitric-acid water solutions was fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the above-mentioned catalyst S, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 100g / L-support was acquired. The amount of rhodium support was 13.33 g/cf (0.47 g/L) (catalyst T).

[0060] Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10

g/L was made to contain as BaO, and the down-stream catalyst U was acquired.

[0061] The beta-zeolite powder 600 section of example of comparison preparation 5SiO₂/aluminum₂O₃ =25, ZSM5 of SiO₂/aluminum₂O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst U, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst V of amount weight of coats 300 g/L-support was acquired.

[0062] The beta-zeolite powder 600 section of example of comparison preparation 6SiO₂/aluminum₂O₃ =25, ZSM5 of SiO₂/aluminum₂O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the catalyst U acquired in the example 4 of a comparison, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst W of amount weight of coats 200 g/L-support was acquired.

[0063] The specification of each catalyst acquired in the above-mentioned examples 1-12 of preparation and the examples 1-6 of comparison preparation is shown in Tables 1 and 2.

[0064]

[Table 1]

調製例	組成	コート量 (g/L)	PM量 (g/L)	備考
1 触媒A	SiO ₂ /Al ₂ O ₃ =15, A型ゼライト [La _{0.85} Pr _{0.15} 0.3Ba _{0.1}][Mn _{0.1} Cr _{0.1} Fe _{0.1} Ni _{0.1}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	120.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
2 触媒E	SiO ₂ /Al ₂ O ₃ =25, B型ゼライト SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, LSY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} Ox Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Zr _{0.79} Ox Al ₂ O ₃ BaO	120.0 10.0 20.0 20.0 44.0 14.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
3 触媒F	SiO ₂ /Al ₂ O ₃ =15, X型ゼライト [La _{0.55} Pr _{0.25} 0.2Ce _{0.05} Ni _{0.05}][Cr _{0.1} Mn _{0.3} Ce _{0.2} Fe _{0.1} Ni _{0.1} Al _{0.05} Ti _{0.05}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	120.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
4 触媒G	SiO ₂ /Al ₂ O ₃ =15, A型ゼライト SiO ₂ /Al ₂ O ₃ =15, X型ゼライト [La _{0.55} Pr _{0.25} 0.2Ce _{0.05} Ni _{0.05}][Cr _{0.1} Mn _{0.3} Ce _{0.2} Fe _{0.1} Ni _{0.1} Al _{0.05} Ti _{0.05}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	30.0 30.0 30.0 180.0 30.0	PM 0.18	触媒貯蔵・放出触媒
5 触媒H	SiO ₂ /Al ₂ O ₃ =15, A型ゼライト SiO ₂ /Al ₂ O ₃ =15, X型ゼライト [La _{0.85} Pr _{0.15} 0.3Ba _{0.1}][Mn _{0.1} Cr _{0.1} Fe _{0.1} Ni _{0.1}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	15.0 15.0 30.0 210.0 30.0	PM 0.21	触媒貯蔵・放出触媒
6 触媒I	SiO ₂ /Al ₂ O ₃ =15, A型ゼライト [La _{0.85} Pr _{0.15} 0.3Ba _{0.1}][Mn _{0.1} Cr _{0.1} Fe _{0.1} Ni _{0.1}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
7 触媒J	SiO ₂ /Al ₂ O ₃ =15, X型ゼライト [La _{0.85} Pr _{0.15} 0.3Ba _{0.1}][Mn _{0.1} Cr _{0.1} Fe _{0.1} Ni _{0.1}]Oy Pd _{0.1} %/La _{0.01} Zr _{0.32} Ce _{0.67} Ox SiO ₂ zol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
8 触媒K	SiO ₂ /Al ₂ O ₃ =25, B型ゼライト SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, LSY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} Ox Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Zr _{0.79} Ox Al ₂ O ₃ BaO	160.0 10.0 10.0 20.0 44.0 14.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
9 触媒L	SiO ₂ /Al ₂ O ₃ =50, B型ゼライト SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} Ox Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Zr _{0.79} Ox Al ₂ O ₃ BaO	180.0 20.0 44.0 14.0 2.0 23.5 15.0 1.5 10.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
10 触媒M	SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, LSY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} Ox Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Zr _{0.79} Ox Al ₂ O ₃ BaO	80.0 180.0 20.0 44.0 14.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層

[0065]
[Table 2]

実施例	組成	コート量 (g/L)	PM量 (g/L)	備考
11 触媒N	SiO ₂ /Al ₂ O ₃ =50, 80.5wt.%, CaO, 1wt.%, β-セライト	180.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ zol.	20.0		
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	11.0		
	Pd2.5%/La0.01Zr0.32Ce0.67Ox	14.0	Pd 5.18	
	Al ₂ O ₃	2.0		
	Rh2%/Zr3wt.%, Al ₂ O ₃	23.5		
12 触媒O	SiO ₂ /Al ₂ O ₃ =25, Pd, 1wt.%, Mn0.1wt.%, Pt0.1wt.%, β-セライト	180.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ /Al ₂ O ₃ =50, Pt0.1%, Rh0.1%, Ca0.1%, ZSM5	20.0		
	SiO ₂ /Al ₂ O ₃ =25, Pt0.5wt.%, Ca0.1wt.%, USY	20.0		
	SiO ₂ zol.	20.0		
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	11.0		
	Pd2.5%/La0.01Zr0.32Ce0.67Ox	14.0	Pd 5.18	
比較 調製例	組成	コート量 (g/L)	PM量 (g/L)	備考
	SiO ₂ /Al ₂ O ₃ =15, A型セライト			セライトのみの 触媒貯蔵・放出触媒
	SiO ₂ zol.			
	[La0.6Sr0.3Ba0.1][Mn0.4Co0.4Fe0.1Al0.1]Oy			セライトのみの 触媒貯蔵・放出触媒
	SiO ₂ zol.			
	Pd0.1%, La0.01Zr0.32Ce0.67Ox			貴金属担持セリウム 触媒貯蔵・放出触媒
4 触媒U	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	44.0		三元触媒 内層: 貴金属成分層 表層: 貴金属成分層
	Pd2.5%/La0.01Zr0.32Ce0.67Ox	11.0		
	Al ₂ O ₃	2.0		
	Rh2%/Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79Ox	15.0	Rh 0.47	
	Al ₂ O ₃	1.5		
5 触媒V	BaO	10.0		炭化水素吸着材と貴 金属成分層の配設を 省略 内層: 貴金属成分層 中層: 貴金属成分層 表層: 炭化水素吸着材
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	44.0		
	Pd2.5%/La0.01Zr0.32Ce0.67Ox	11.0	Pd 5.18	
	Al ₂ O ₃	2.0		
	Rh2%/Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79Ox	15.0	Rh 0.47	
6 触媒W	SiO ₂ /Al ₂ O ₃ =25, Pt, 1wt.%, Mn0.1wt.%, Pd0.1wt.%, β-セライト	180.0		炭化水素吸着材のみの 触媒
	SiO ₂ /Al ₂ O ₃ =50, Pt0.1%, Rh0.1%, Ca0.1%, ZSM5	40.0		
	SiO ₂ /Al ₂ O ₃ =25, Pt0.5wt.%, Ca0.1wt.%, USY	20.0		
	SiO ₂ zol.	20.0		
	SiO ₂ /Al ₂ O ₃ =25, β-セライト	120.0		
	SiO ₂ /Al ₂ O ₃ =50, ZSM5	40.0		

[0066] examples 1-12 and the examples 1-7 of a comparison -- the following durable conditions performed durability for each catalyst acquired in said examples 1-12 of preparation, and the examples 1-6 of comparison preparation.

[0067]

Durable conditions Engine displacement 3000 cc Fuel Unleaded gasoline Catalyst inlet gas temperature 500 degrees C Durable time amount 50 hours Inlet-port gas presentation CO 0.5**0.1% O₂ 0.5**0.1% HC About 1100 ppm NO 1300 ppm CO₂ 15% A/F fluctuation 2750 times (65 seconds/time of periods) Period: A/F=14.6 55 seconds Fuel cut 5 seconds Rich Spike 5 seconds (CO=2%)

[0068] Subsequently, it installed in the evaluation system which shows each catalyst after durability to the catalyst arrangement and drawing 1 which are shown in the following table 3, and the catalyst equipment for exhaust gas purification was obtained. The approach of purifying exhaust gas was performed on condition that the following using each equipment.

[0069]

Purification evaluation conditions Engine displacement Nissan Motor Co., Ltd. make V type 6-cylinder

3.3L Fuel Unleaded gasoline Evaluation mode LA4-CH (A-bag)

[0070] The evaluation result (emission value) measured on the above-mentioned purification conditions about each example and the example of a comparison is shown in Table 3.

[0071] However, a cold HC discharge arranges TWC to the catalyst arrangement 1, and measures base emission. TWC is arranged to the catalyst arrangement 1, it arranges each catalyst to arrangement 2 and 3, and the cold HC amount of adsorption is taken as difference with the above-mentioned base emission (for [of LA4Abag] 0 to 60 seconds). The amount of non-purified desorption HC considers difference with the base emission after 60 second as the non-purified desorption HC to the above-mentioned cold HC amount of adsorption. Moreover, [Equation 1]

$$\text{脱離HC浄化率} = \frac{[\text{コールドHC吸着量}] - [\text{未浄化脱離HC量}]}{[\text{コールドHC吸着量}]} \times 100$$

The amount of desorption HC purification = it measured as an amount of cold HC amount-of-adsorption-non-purified desorption HC.

[0072]

[Table 3]

	触媒配置			コールドHC 排出量 (g/test)	コールドHC 吸着量 (g/test)	未浄化 脱離HC量 (g/test)	脱離HC 浄化率 (%)	脱離HC 浄化量 (g/test)
	1	2	3					
実施例 1	TWC	触媒A	触媒E	1.22	0.915	0.706	22.8	0.209
実施例 2	TWC	触媒F	触媒E	1.22	0.915	0.705	23.0	0.210
実施例 3	TWC	触媒G	触媒E	1.22	0.915	0.704	23.1	0.211
実施例 4	TWC	触媒H	触媒E	1.22	0.915	0.702	23.3	0.213
実施例 5	TWC	触媒I	触媒E	1.22	0.915	0.703	23.2	0.212
実施例 6	TWC	触媒J	触媒E	1.22	0.915	0.700	23.5	0.215
実施例 7	TWC	触媒A	触媒K	1.22	0.927	0.708	23.6	0.219
実施例 8	TWC	触媒F	触媒L	1.22	0.939	0.719	23.4	0.220
実施例 9	TWC	触媒G	触媒M	1.22	0.903	0.683	24.4	0.220
実施例 10	TWC	触媒H	触媒N	1.22	0.939	0.718	23.5	0.221
実施例 11	TWC	触媒I	触媒O	1.22	0.952	0.731	23.7	0.221
実施例 12	TWC	触媒J	触媒E	1.22	0.915	0.695	23.9	0.219
比較例 1	TWC	なし	触媒E	1.22	0.915	0.714	22.0	0.201
比較例 2	TWC	触媒P	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 3	TWC	触媒Q	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 4	TWC	触媒R	触媒E	1.22	0.915	0.713	22.0	0.202
比較例 5	TWC	触媒A	触媒U	1.22	0.915	0.910	0.55	0.005
比較例 6	TWC	触媒A	触媒V	1.22	0.915	0.759	17.0	0.156
比較例 7	TWC	触媒A	触媒W	1.22	0.915	0.915	0.000	0.000

[0073]

[Effect of the Invention] The exhaust gas purification approach according to claim 1 combines a catalyst with oxygen storage / emission ability, and the catalyst which has hydrocarbon adsorption and decontamination capacity. By supplying oxygen required for purification in case the catalyst which adsorbed the hydrocarbon in the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine is desorbed from a hydrocarbon by the rise of catalyst bed temperature The purification engine performance of a hydrocarbon can be improved and the hydrocarbon discharged with un-purifying can be reduced sharply.

[0074] It adds to the above-mentioned effectiveness and the exhaust gas purification approach according to claim 2 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. When a ratio uses 20 or less A mold and an X type zeolite Emission with separation and adsorption is easily controllable by the temperature

change of a catalyst bed alternatively [oxygen], in case it is desorbed from a hydrocarbon by the rise of the catalyst bed temperature which adsorbed the hydrocarbon, oxygen required for purification can be supplied and the purification engine performance can be improved.

[0075] The exhaust gas purification approach according to claim 3 can control that the zeolite used as oxygen adsorption material is destroyed by heat in addition to the above-mentioned effectiveness, and this zeolite can aim at maintenance of the engine performance which separates, adsorbs and emits oxygen.

[0076] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 4 can aim at improvement in the engine performance by which this catalyst dissociates and adsorbs oxygen, when thermal resistance contains an oxygen migratory high, high ingredient.

[0077] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 5 can aim at improvement in the engine performance to which this catalyst emits oxygen.

[0078] In addition to the above-mentioned effectiveness, by combining various hydrocarbon adsorption material, the exhaust gas purification approach according to claim 6 adsorbs the hydrocarbon kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and can improve the decontamination capacity of the hydrocarbon moreover desorbed from a noble-metals component by contacting hydrocarbon adsorption material.

[0079] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 7 adsorbs HC kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and moreover, since the structural change and performance degradation after durability are small, it can attain delay-ization of a desorption rate.

[0080] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 8 can control the catalyst performance degradation resulting from reduction of a catalyst component.

[0081] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 9 improves the purification engine performance further, and can control the catalyst performance degradation resulting from poisoning of a catalyst component.

[0082] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 10 improves, carries out sintering control of the low-temperature activity of palladium further, and can improve endurance.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the exhaust gas purification approach which can purify HC efficiently especially among the hydrocarbon in the exhaust gas discharged from internal combustion engines, such as an automobile, at the time of the low temperature immediately after engine starting ("HC" is called hereafter), a carbon monoxide ("CO" is called below), and a nitriding oxide ("NOx" is called hereafter) about the exhaust gas purification approach.

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PRIOR ART

[Description of the Prior Art] the approach of desorb, after use HC adsorption material, store temporarily for the purpose of reduction of the hydrocarbon in the exhaust gas discharge at the time of the low temperature immediately after engine starting ("cold HC" be call hereafter) and activate a three way component catalyst from before, since the catalyst for exhaust gas purification do not have the enough endurance under an elevated temperature, a catalyst deteriorate and decontamination capacity fall remarkably, and purify with this three way component catalyst be examine.

[0003] As a catalyst for exhaust gas purification using this HC adsorption material, there are some which are indicated by JP,6-74019,A, JP,7-144119,A, JP,6-142457,A, JP,5-59942,A, or JP,7-102957,A, for example.

[0004] After establishing bypass passage in exhaust air passage, making JP,6-74019,A once stick to HC adsorption material which has arranged HC discharged at the time of cold one immediately after engine starting to bypass passage, switching exhaust air passage to it after that and activating a down-stream three way component catalyst, the system which purifies gradually HC desorbed through HC adsorption catalyst from a part of exhaust gas with a latter three way component catalyst is proposed.

[0005] In JP,7-144119,A, heat is taken by the three way component catalyst of the preceding paragraph at the time of cold one immediately after engine starting, the adsorption effectiveness of HC adsorption material of the middle is raised, and the system which makes heat transfer of the heat of reaction easy to carry out to a latter three way component catalyst through HC adsorption material of the middle which carried out tandem arrangement in after three way component catalyst activation of the preceding paragraph, and promotes purification with a latter three way component catalyst is proposed.

[0006] In case HC to which it stuck in the low-temperature region ****s, the preheating of the exhaust gas including Desorption HC is carried out by the heat exchanger, and the cold HC adsorption treatment system which promotes purification with a three way component catalyst is proposed by JP,6-142457,A.

[0007] By switching the passage of the exhaust gas by catalyst arrangement and the bulb, the temperature up of HC adsorption material is made slow, and the system which improves the adsorption effectiveness of cold HC is proposed by JP,5-59942,A.

[0008] Moreover, in order to improve the purification engine performance of a latter oxidation and three way component catalyst, air is supplied between the three way component catalyst of the preceding paragraph, and HC adsorption material of the middle, and the system which promotes activation of a latter oxidation and three way component catalyst is proposed by JP,7-102957,A.

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EFFECT OF THE INVENTION

[Effect of the Invention] The exhaust gas purification approach according to claim 1 combines a catalyst with oxygen storage / emission ability, and the catalyst which has hydrocarbon adsorption and decontamination capacity. By supplying oxygen required for purification in case the catalyst which adsorbed the hydrocarbon in the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine is desorbed from a hydrocarbon by the rise of catalyst bed temperature The purification engine performance of a hydrocarbon can be improved and the hydrocarbon discharged with un-purifying can be reduced sharply.

[0074] It adds to the above-mentioned effectiveness and the exhaust gas purification approach according to claim 2 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. When a ratio uses 20 or less A mold and an X type zeolite Emission with separation and adsorption is easily controllable by the temperature change of a catalyst bed alternatively [oxygen], in case it is desorbed from a hydrocarbon by the rise of the catalyst bed temperature which adsorbed the hydrocarbon, oxygen required for purification can be supplied and the purification engine performance can be improved.

[0075] The exhaust gas purification approach according to claim 3 can control that the zeolite used as oxygen adsorption material is destroyed by heat in addition to the above-mentioned effectiveness, and this zeolite can aim at maintenance of the engine performance which separates, adsorbs and emits oxygen.

[0076] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 4 can aim at improvement in the engine performance by which this catalyst dissociates and adsorbs oxygen, when thermal resistance contains an oxygen migratory high, high ingredient.

[0077] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 5 can aim at improvement in the engine performance to which this catalyst emits oxygen.

[0078] In addition to the above-mentioned effectiveness, by combining various hydrocarbon adsorption material, the exhaust gas purification approach according to claim 6 adsorbs the hydrocarbon kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and can improve the decontamination capacity of the hydrocarbon moreover desorbed from a noble-metals component by contacting hydrocarbon adsorption material.

[0079] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 7 adsorbs HC kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and moreover, since the structural change and performance degradation after durability are small, it can attain delay-ization of a desorption rate.

[0080] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 8 can control the catalyst performance degradation resulting from reduction of a catalyst component.

[0081] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 9 improves the purification engine performance further, and can control the catalyst

performance degradation resulting from poisoning of a catalyst component.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, HC adsorption effectiveness falls after durability, moreover, since the conventional system using HC adsorption material indicated in said official report of the endurance of HC adsorption material is inadequate, before a latter three way component catalyst is activated, HC will **** and emission will be worsened in it.

[0010] Then, in order to attain improvement in adsorption effectiveness and the formation of desorption delay of HC adsorption material, the heat exchanger for the method of bypassing elevated-temperature gas or three way component catalyst pre-heating is used, but while a system configuration makes it complicated, sufficient effectiveness is not acquired, but since cost goes up remarkably, moreover, HC adsorption material with high endurance and adsorption effectiveness is desired.

[0011] In order to use noble metals so much in order to maintain the high purification engine performance from the first stage to until after durability, or to aim at promotion of purification of early activation and Desorption HC, especially the three way component catalyst aiming at purification of HC desorbed from HC adsorption material introduces air, and is shining and carrying out it. For this reason, although a catalyst from which the purification engine performance in which the amount of noble metals to be used is high at least is obtained was desired, when noble metals were reduced, endurance became inadequate and after durability had the problem that the catalytic activity and the purification engine performance in a low-temperature region got worse.

[0012] Therefore, in purifying low-temperature exhaust gas, the purpose of this invention is to offer the exhaust gas purification approach which shows the low-temperature activity and the purification engine performance which endurance improved and the conventional catalyst was excelled especially after elevated-temperature durability, and HC purification effectiveness in which it excelled especially.

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MEANS

[Means for Solving the Problem] In purification of the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as a result of inquiring, in order that this invention persons may solve the above-mentioned technical problem The catalyst which has hydrocarbon adsorption and decontamination capacity for the catalyst which has oxygen storage / emission ability in the upstream of exhaust gas in the downstream is arranged. When the catalyst of the downstream ****ed and purified a hydrocarbon, HC purification effectiveness at the time of cold HC to which it stuck ****ing reached [being improved and maintained remarkably and] a header and this invention by supplying oxygen to the catalyst of the downstream from the catalyst of the upstream.

[0014] In the exhaust gas purification approach according to claim 1 purifying low-temperature exhaust gas The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and it is characterized by adjusting said bulb according to the temperature in the catalyst bed of the catalyst of the upstream.

[0015] For the exhaust gas purification approach according to claim 2, the catalyst arranged to the upstream in the exhaust gas purification approach according to claim 1 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. It is characterized by a ratio containing 20 or less A mold and X zeolite.

[0016] The exhaust gas purification approach according to claim 3 is characterized by preventing flowing into the catalyst to which the bulb installed in the upstream of this catalyst was operated, exhaust gas passage was changed, and exhaust gas has arranged the temperature of 400 degrees C or more to the upstream concerned, when the temperature in the catalyst bed of the catalyst arranged to the upstream reaches 400 degrees C in the exhaust gas purification approach according to claim 1 or 2.

[0017] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 4 -- claims 1-3 -- the catalyst arranged to the upstream -- the next empirical formula: [A] [B] Oy (the element more than a kind chosen from the group which A becomes from La, Sr, Ba, Pb, Nd, and Ce among a formula, and B) an oxygen atomic number required for the element more than a kind chosen from the group which consists of aluminum, Ti, Cr, Mn, Co, Fe, and nickel, and O to show oxygen, and for y satisfy the valence of each element -- being shown -- it is characterized by containing the multiple oxide of the perovskite type structure expressed.

[0018] the exhaust gas purification approach according to claim 5 -- claims 1-4 -- in the exhaust gas

purification approach given [one of] in a term, the catalyst arranged to the upstream is characterized by containing the cerium oxide which supported platinum and/or palladium.

[0019] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 6 -- claims 1-5 -- The zeolite more than a kind chosen from the group which the catalyst arranged to the downstream becomes from ZSM5, USY, and beta-zeolite as hydrocarbon adsorption material, It is characterized by containing the metal more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound.

[0020] The exhaust gas purification approach according to claim 7 is characterized by hydrocarbon adsorption material containing the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium in the exhaust gas purification approach according to claim 6.

[0021] the element more than a kind chosen from the group to which the exhaust gas purification approach according to claim 8 becomes the upper part of a hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in the exhaust gas purification approach according to claim 7 -- metal conversion -- 1-40-mol % and a cerium -- 60-98-mol % -- it is characterized by arranging the catalyst component layer containing the included cerium oxide.

[0022] The exhaust gas purification approach according to claim 9 is set to the exhaust gas purification approach according to claim 8. In the upper part of the catalyst component layer containing the palladium arranged in the upper part of a hydrocarbon adsorption material layer Furthermore, the zirconic acid ghost which contains a 1-30 mol % zirconium for a kind chosen from the group which consists of platinum, a rhodium, a cerium, neodium, and a lanthanum 70 to 98% by metal conversion, The exhaust gas purification approach according to claim 8 characterized by arranging the catalyst component layer containing an activated alumina.

[0023] The exhaust gas purification approach according to claim 10 is characterized by arranging the three way component catalyst which was chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from alkali metal and alkaline earth metal and which a kind contains at least in the exhaust gas purification approach according to claim 8 or 9.

[0024]

[Embodiment of the Invention] In purifying the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as the exhaust gas purification approach of this invention The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and said bulb can improve the desorption hydrocarbon purification effectiveness of the catalyst of this downstream by considering as the configuration adjusted according to the temperature in the catalyst bed of the catalyst of the upstream.

[0025] The oxygen adsorption material ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains is SiO₂ / aluminum 2O₃ which can dissociate and adsorb oxygen alternatively out of low-temperature exhaust gas. 20 or less A mold and an X type zeolite have an effective ratio. Catalyst bed temperature separates and stores the oxygen in exhaust gas alternatively from a room temperature in a 200-degree C temperature region, and can emit oxygen in a 200 to 400

degrees C temperature region, the catalyst which made this zeolite contain can supply oxygen efficiently, in case the catalyst of the downstream ****s and purifies the hydrocarbon to which it stuck from low-temperature exhaust gas, and it can raise HC purification effectiveness of noble metals. As for the amount, per [catalyst 1L / 10g-300g] are desirable from the point of the improvement in the engine performance.

[0026] Moreover, although the bulb installed in the upstream of this catalyst is operated and exhaust gas passage is changed when the temperature in the catalyst bed of this upstream (a thermometric element is installed into the catalyst bed concerned, and temperature is detected) reaches 400 degrees C, this is for preventing that exhaust gas with a temperature of 400 degrees C or more flows into oxygen adsorption material, and preventing the structure destruction by the heat of this zeolite.

[0027] moreover -- as the ingredient which was excellent in thermal resistance in order that the catalyst arranged to this upstream might emit oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more -- the next empirical formula: [A] [B] Oy (A) The element more than a kind chosen from the group which consists of La, Sr, Ba, Pb, Nd, and Ce, and B an oxygen atomic number required for the element more than a kind chosen from the group which consists of AL, Ti, Cr, Mn, Co, Fe, and Ne, and O to show oxygen, and for y satisfy the valence of each element -- being shown -- the multiple oxide of the oxygen migratory high perovskite type structure expressed can be contained. By this, the degradation of the oxygen adsorption material slack zeolite arranged to this upstream can be compensated, and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved further.

[0028] Furthermore, since the catalyst arranged to this upstream promotes the operation which emits oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more, the cerium oxide which supported platinum and/or palladium can be made to contain. By making this catalyst contain platinum and/or a palladium support cerium oxide, the endurance of the catalyst arranged to the upstream improves and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved over a long period of time.

[0029] As amount of the sum total used of the ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains, they are the above, and SiO₂ / aluminum 2O₃. Per [upper catalyst 1L / 10g-300g] are desirable combining the cerium oxide with which the ratio supported 20 or less A mold and an X type zeolite, the multiple oxide of perovskite type structure, and platinum and/or palladium. The adsorption engine performance is saturated with less than 10g, and the amount of the ingredient used which has oxygen storage / supply ability is not economically effective at it, even if the adsorption engine performance is not fully discovered and exceeds 300g conversely.

[0030] Moreover, as an ingredient which adsorbs the hydrocarbon discharged in the low-temperature region arranged at the downstream, they are SiO₂ / aluminum 2O₃. The various hydrocarbons discharged in a low-temperature region can be efficiently adsorbed by using more than a kind chosen from the group which a ratio becomes from 20 or more ZSM5, USY(s), and beta-zeolites. As for the amount of the hydrocarbon adsorption material used, per [catalyst 1L / 10g-300g] are desirable. The adsorption engine performance is saturated with less than 10g, and the amount of the hydrocarbon adsorption material used is not economically effective at it, even if the adsorption engine performance is not fully discovered and exceeds 300g conversely. Furthermore, since the hydrocarbon desorbed from this hydrocarbon adsorption material is purified, the hydrocarbon from which it is desorbed with the rise of catalyst bed temperature can be efficiently purified by containing the element more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound. 1g-30g, and an activated alumina are [10g-300g, and Seria oxide / 5g-100g, and a zirconic acid ghost / 5g-100g, and a barium compound] desirable [the amount / per / catalyst 1L / and noble metals / that they are 1g-50g] from the point which purifies Desorption HC efficiently.

[0031] Furthermore, since the structural stability under the elevated temperature of hydrocarbon adsorption material (thermal resistance), adsorption capacity cold [HC], and HC desorption control engine performance at the time of a temperature rise are improved, the element more than a kind chosen

from the group which consists of platinum, palladium, Lnn, boron, magnesium, and calcium can be contained. The content of this element is 10 % of the weight from 0.1 % of the weight to HC adsorption material. If it is less than 0.1 % of the weight, sufficient amelioration effectiveness will not be acquired, but if it is conversely used mostly from 10 % of the weight, the pore of a zeolite will blockade and HC adsorption capacity will fall.

[0032] furthermore, the element more than a kind chosen from the group which becomes the upper part of this hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in order to improve the purification effectiveness at the time of HC to which it stuck by hydrocarbon adsorption material ****ing -- metal conversion -- a 1-40 mol % cerium -- 60-98-mol % -- the catalyst component layer containing the included cerium oxide can be arranged. In order to raise the purification engine performance and endurance of palladium especially, in a palladium content catalyst component layer the element more than a kind chosen from the group which consists of a zirconium, neodium, and a lanthanum -- metal conversion -- a 1-40 mol % cerium -- 60-98-mol % -- by making the included cerium oxide contain Since the high cerium oxide of oxygen occlusion ability becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidization condition of palladium, and the fall of the catalyst ability of palladium can be controlled. As for the amount of this palladium used, it is desirable from the point of the purification engine performance that they are per [catalyst 1L / 1g-30g]. The amount of this cerium oxide used is per [catalyst 1L / 5-100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0033] furthermore, the element more than a kind chosen from the group which becomes the upper part of the catalyst component layer containing palladium from platinum, a rhodium, a cerium, neodium, and a lanthanum in order to improve the poisoning-proof nature and the purification engine performance of palladium -- metal conversion -- a 1-30 mol % zirconium -- 70-98-mol % -- the catalyst component layer containing the included zirconic acid ghost and an activated alumina can be arranged. As a base material with which said platinum and rhodium are supported, in order to raise the endurance of platinum or a rhodium, a zirconic acid ghost is suitable. Since the high cerium content zirconic acid ghost of oxygen occlusion ability especially becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidization condition of platinum or a rhodium, and the fall of the catalyst ability of platinum or a rhodium can be controlled.

[0034] The cerium content of this zirconic acid ghost is 0.01-mol % to 30-mol %. Less than [0.01 mol %], a cerium content is ZrO₂. ZrO₂ of the element which was not different from a case and was described above If the amelioration effectiveness by the oxygen occlusion ability of a cerium does not show up and a cerium content exceeds 30-mol %, a BET specific surface area and thermal stability will fall [this effectiveness] to saturation or reverse. The amount of the zirconic acid ghost used is per [catalyst 1L / 5-100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0035] Moreover, since the low-temperature activity of palladium is improved, the three way component catalyst containing alkali metal and/or alkaline earth metal can be arranged. There are a potassium, calcium, strontium, barium, sodium, magnesium, an yttrium, a lanthanum, etc. in these metals. The content of this element is among [1-40g] catalyst 1L. In less than 1g, neither relaxation of adsorption poisoning to the noble metals of HC nor sintering of palladium can be controlled, but even if it exceeds 40g, the capable increase-in-quantity effectiveness is not acquired, but the engine performance is reduced conversely.

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EXAMPLE

[Example] The example of preparation, a following example, and the following example of a comparison explain this invention. The section is weight ***** as long as there is especially no display.

[0037] A mold zeolite powder of example of preparation 1SiO₂/aluminum₂O₃ =15 The 400 sections, Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy Perovskite mold multiple oxide powder The 250 sections, The palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1% of palladium support concentration The 250 sections, With the 500 sections, 2000g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst A of amount weight of coats 300 g/L-support was acquired. The amount of palladium support was 2.12g/cf (0.075 g/L).

[0038] The 200 sections and USY of SiO₂/aluminum₂O₃ =25 for the 600 sections and ZSM5 of SiO₂/aluminum₂O₃ =50 The 100 sections, [beta-zeolite powder of example of preparation 2SiO₂/aluminum₂O₃ =25] With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst of amount weight of coats 200 g/L-support was acquired (catalyst B).

[0039] After sinking the palladium nitrate water solution into the alumina powder (powder A) containing cerium 3 mol % (it converts into CeO₂ and is 8.7 % of the weight), zirconium 3 mol % (it converts into ZrO₂ and is 6.3 % of the weight), and lanthanum 2 mol % (it converts into La₂O₃, and is 5.5 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support alumina powder (powder B) was obtained. Pd concentration of this powder B was 11 % of the weight.

[0040] After sinking the palladium nitrate water solution into the cerium oxide powder (powder C) containing lanthanum 1 mol % (it converts into La₂O₃, and is 2 % of the weight), and zirconium 32 mol % (it converts into ZrO₂ and is 25 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder (powder D) was obtained. Pd concentration of this powder D was 2.5 % of the weight.

[0041] The above-mentioned powder B880g, powder D280g, 40g of activated aluminas, and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst B, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 260g / L-support was acquired. The amount of palladium support was 146.67g/cf (5.18 g/L) (catalyst C).

[0042] Subsequently, after sinking a nitric-acid rhodium water solution into the activated-alumina object powder (powder E) which supported 3 % of the weight of Zr and drying at 150 degrees C for 12 hours, it calcinates at 400 degrees C for 1 hour, and it is 3 % of the weight-aluminum 2O₃ of Rh support Zr. Powder (powder F) was obtained. Rh concentration of this powder F was 2.0 % of the weight.

[0043] The 300 sections, the activated-alumina 30 section, and 1500g of nitric-acid water solutions were fed into the magnetic ball mill for the 470 sections and zirconic acid ghost powder (La1 mol %, Ce20 mol %, and Zr79 mol %) (powder F), the above-mentioned powder E was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst C, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 300g / L-support was acquired. The amount of rhodium support was 13.33 g/cf (0.47 g/L) (catalyst D).

[0044] E Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10 g/L was made to contain as BaO, and the down-stream catalyst was acquired.

[0045] In the A mold zeolite powder 400 section of example of preparation 3SiO₂/aluminum₂ O₃ =15, instead of, The X type zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 400 sections.

Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.5} Sr_{0.2} Ba_{0.2} Ce_{0.05}Nd_{0.05}] and [Cr_{0.1} Mn_{0.3} Fe_{0.1} nickel_{0.1} aluminum_{0.05}Ti_{0.05}] The perovskite mold multiple oxide powder of Oy is made into the 250 sections. Except having used the amount of the platinum support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of platinum support concentration as the 250 sections, the upper catalyst F was acquired according to the example 1.

[0046] In the A mold zeolite powder 400 section of example of preparation 4SiO₂/aluminum₂ O₃ =15, instead of, The 100 sections and the X type zeolite powder of SiO₂/aluminum₂O₃ =15 are made into the 100 sections for A mold zeolite powder of aluminum₂O₃/aluminum₂ O₃ =15. Empirical formula:

[La_{0.6} Sr_{0.3}Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.5} Sr_{0.2} Ba_{0.2} Ce_{0.05}Nd_{0.05}] and [Cr_{0.1} Mn_{0.3} Fe_{0.1} nickel_{0.1} aluminum_{0.05}Ti_{0.05}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 600 sections, the upper catalyst G was acquired according to the example 1.

[0047] In the A mold zeolite powder 400 section of example of preparation 5SiO₂/aluminum₂ O₃ =15, instead of, The 50 sections and the X type zeolite powder of SiO₂/aluminum₂ O₃=15 are made into the 50 sections for A mold zeolite powder of SiO₂/aluminum₂ O₃ =15. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 700 sections, the upper catalyst H was acquired according to the example 1.

[0048] In the A mold zeolite powder 400 section of example of preparation 6SiO₂/aluminum₂ O₃ =15, instead of, A mold zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 50 sections. Empirical formula: [La_{0.6}Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy It considers as the perovskite mold multiple oxide powder 50 section. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}Ox) powder of 0.1 % of the weight of palladium support concentration as the 900 sections, the upper catalyst H was acquired according to the example 1.

[0049] In the A mold zeolite powder 400 section of example of preparation 7SiO₂/aluminum₂ O₃ =15, instead of, The X type zeolite powder of SiO₂/aluminum₂ O₃ =15 is made into the 50 sections. Empirical formula: [La_{0.6}Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, Empirical formula [La_{0.9} Sr_{0.1}] Oy Perovskite

mold multiple oxide powder is made into the 50 sections. Except having used the amount of the palladium support cerium oxide ($\text{La}_{0.01}\text{Zr}_{0.32}\text{Ce}_{0.67}\text{O}_x$) powder of 0.1 % of the weight of palladium support concentration as the 800 sections, the upper catalyst J was acquired according to the example 1. [0050] The beta-zeolite powder 600 section of example of preparation $8\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ In the 200 sections and the USY100 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, instead of, According to the example 2, the down-stream catalyst K was acquired except having used [the amount of beta-zeolite powder of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$] the 50 sections and the amount of USY of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ for the 800 sections and the amount of ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ as the 50 sections.

[0051] In the beta-zeolite powder 600 section of example of preparation $9\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, instead of, According to the example 2, the down-stream catalyst L was further acquired except not using ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$, and USY of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, using the amount of beta-zeolite powder of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ as the 900 sections.

[0052] ZSM5 of example of preparation $10\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ The 200 sections, The USY100 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ is replaced. ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ The 400 sections, According to the example 2, the down-stream catalyst M was acquired except not using beta-zeolite powder of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ further, using the amount of USY of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ as the 500 sections.

[0053] According to the example 9, the down-stream catalyst N was acquired except having used the beta-zeolite 900 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ containing 0.5 % of the weight of boron, and 0.1 % of the weight of calcium instead of the beta-zeolite powder 900 section of example of preparation $11\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$.

[0054] The beta-zeolite powder 600 section of example of preparation $12\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ In the 200 sections and the USY100 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$, instead of, The beta-zeolite 700 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ containing 0.1 % of the weight of Linn, 0.1 % of the weight of magnesium, and 0.1 % of the weight of palladium, ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=50$ containing 0.1 % of the weight of platinum, 0.1 % of the weight of boron, and 0.1 % of the weight of calcium The 100 sections, According to the example 9, the down-stream catalyst O was acquired except having used the USY100 section of $\text{SiO}_2/\text{aluminum}_2\text{O}_3=25$ containing 0.5 % of the weight of Linn, and 0.1 % of the weight of calcium.

[0055] According to the example 1, the upper catalyst P was acquired except having used only the A mold zeolite powder 900 section of example of comparison preparation $1\text{SiO}_2/\text{aluminum}_2\text{O}_3=15$, and the silica sol (SiO_2 as concentration 20%) 500 section.

[0056] According to the example 1, the upper catalyst Q was acquired except having used only the example of comparison preparation $2[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}][\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{aluminum}_{0.1}]$ Oy powder 900 section, and the silica sol (SiO_2 as concentration 20%) 500 section.

[0057] According to the example 1, the upper catalyst R was acquired except having used only the palladium support cerium oxide ($\text{La}_{0.01}\text{Zr}_{0.32}\text{Ce}_{0.67}\text{O}_x$) powder 900 section of 0.1 % of the weight of example of comparison preparation 3 palladium support concentration, and the silica sol (SiO_2 as concentration 20%) 500 section.

[0058] Powder B880g and powder D280g which was obtained in the example of comparison preparation 4 example 2, and 40g of activated aluminas and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 60g / L-support was acquired. The amount of palladium support was 146.67g/cf (5.18 g/L) (catalyst S).

[0059] Subsequently, with the powder E470 section obtained in the example 2, the zirconic acid ghost powder (powder F) 300 section ($\text{La}_{1\text{ mol \%}}$, $\text{Ce}_{20\text{ mol \%}}$, and $\text{Zr}_{79\text{ mol \%}}$), and the activated-alumina 30 section, 1500g of nitric-acid water solutions was fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the above-mentioned

catalyst S, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 100g / L-support was acquired. The amount of rhodium support was 13.33 g/cf (0.47 g/L) (catalyst T).

[0060] Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10 g/L was made to contain as BaO, and the down-stream catalyst U was acquired.

[0061] The beta-zeolite powder 600 section of example of comparison preparation 5SiO₂/aluminum₂O₃ =25, ZSM5 of SiO₂/aluminum₂O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst U, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst V of amount weight of coats 300 g/L-support was acquired.

[0062] The beta-zeolite powder 600 section of example of comparison preparation 6SiO₂/aluminum₂O₃ =25, ZSM5 of SiO₂/aluminum₂O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the catalyst U acquired in the example 4 of a comparison, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst W of amount weight of coats 200 g/L-support was acquired.

[0063] The specification of each catalyst acquired in the above-mentioned examples 1-12 of preparation and the examples 1-6 of comparison preparation is shown in Tables 1 and 2.

[0064]

[Table 1]

[0065]

[Table 2]

実施例	組成	コート量 (g/L)	PM量 (g/L)	備考
11 触媒N	SiO ₂ /Al ₂ O ₃ =50, 80.5wt.%, CaO, 1wt.%, β-セライト	180.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ sol.	20.0		
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	11.0		
	Pd2.5%, La0.01Zr0.32Ce0.67O _x	14.0	Pd 5.18	
	Al ₂ O ₃	2.0		
	Rh2%, Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79O _x	15.0	Rh 0.47	
12 触媒O	SiO ₂ /Al ₂ O ₃ =25, Pd, 1wt.%, MgO, 1wt.%, PtO, 1wt.%, β-セライト	100.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ /Al ₂ O ₃ =50, Pt0.1%, B0.1%, Ca0.1%, ZSM5	20.0		
	SiO ₂ /Al ₂ O ₃ =25, Pt0.5wt.%, Ca0.1wt.%, USY	20.0		
	SiO ₂ sol.	20.0		
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	11.0		
	Pd2.5%, La0.01Zr0.32Ce0.67O _x	14.0	Pd 5.18	
	Al ₂ O ₃	2.0		
比較 調製例	Rh2%, Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79O _x	15.0	Rh 0.47	
	Al ₂ O ₃	1.5		
	BaO	10.0		
	組成	コート量 (g/L)	PM量 (g/L)	
	1 触媒P	SiO ₂ /Al ₂ O ₃ =15, A型セライト SiO ₂ sol.		
	2 触媒O	[La0.6Sr0.3B0.1][Mn0.4Cr0.4Fe0.1Al0.1]O _y SiO ₂ sol.		
4 触媒U	Pd0.1%, La0.01Zr0.32Ce0.67O _x SiO ₂ sol.			三元触媒 内層: 貴金属成分層 表層: 貴金属成分層
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	11.0		
	Pd2.5%, La0.01Zr0.32Ce0.67O _x	14.0	Pd 5.18	
	Al ₂ O ₃	2.0		
	Rh2%, Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79O _x	15.0	Rh 0.47	
	Al ₂ O ₃	1.5		
5 触媒V	BaO	10.0		
	Pd11%, Ce3mol.%, Zr3mol.%, La2mol.%, Al ₂ O ₃	44.0		炭化水素吸着材と貴 金属成分層の配向を 逆転 内層: 貴金属成分層 中層: 貴金属成分層 表層: 炭化水素吸着材
	Pd2.5%, La0.01Zr0.32Ce0.67O _x	11.0	Pd 5.18	
	Al ₂ O ₃	2.0		
	Rh2%, Zr3wt.%, Al ₂ O ₃	23.5		
	La0.01Ce0.22Zr0.79O _x	15.0	Rh 0.47	
	Al ₂ O ₃	1.5		
	BaO	10.0		
6 触媒W	SiO ₂ /Al ₂ O ₃ =25, β-セライト	120.0		炭化水素吸着材のみ の触媒
	SiO ₂ /Al ₂ O ₃ =50, ZSM5	40.0		
	SiO ₂ /Al ₂ O ₃ =25, USY	20.0		
	SiO ₂ sol.	20.0		

[0066] examples 1-12 and the examples 1-7 of a comparison -- the following durable conditions performed durability for each catalyst acquired in said examples 1-12 of preparation, and the examples 1-6 of comparison preparation.

[0067]

Durable conditions Engine displacement 3000 cc Fuel Unleaded gasoline Catalyst inlet gas temperature 500 degrees C Durable time amount 50 hours Inlet-port gas presentation CO 0.5**0.1% O₂ 0.5**0.1% HC About 1100 ppm NO 1300 ppm CO₂ 15% A/F fluctuation 2750 times (65 seconds/time of periods) Period: A/F=14.6 55 seconds Fuel cut 5 seconds Rich Spike 5 seconds (CO=2%)

[0068] Subsequently, it installed in the evaluation system which shows each catalyst after durability to the catalyst arrangement and drawing 1 which are shown in the following table 3, and the catalyst equipment for exhaust gas purification was obtained. The approach of purifying exhaust gas was performed on condition that the following using each equipment.

[0069]

Purification evaluation conditions Engine displacement Nissan Motor Co., Ltd. make V type 6-cylinder

3.3L Fuel Unleaded gasoline Evaluation mode LA4-CH (A-bag)

[0070] The evaluation result (emission value) measured on the above-mentioned purification conditions about each example and the example of a comparison is shown in Table 3.

[0071] However, a cold HC discharge arranges TWC to the catalyst arrangement 1, and measures base emission. TWC is arranged to the catalyst arrangement 1, it arranges each catalyst to arrangement 2 and 3, and the cold HC amount of adsorption is taken as difference with the above-mentioned base emission (for [of LA4Abag] 0 to 60 seconds). The amount of non-purified desorption HC considers difference with the base emission after 60 second as the non-purified desorption HC to the above-mentioned cold HC amount of adsorption. Moreover, [Equation 1]

$$\text{脱離HC浄化率} = \frac{[\text{コールドHC吸着量}] - [\text{未浄化脱離HC量}]}{[\text{コールドHC吸着量}]} \times 100$$

The amount of desorption HC purification = it measured as an amount of cold HC amount-of-adsorption-non-purified desorption HC.

[0072]

[Table 3]

	触媒配置			コールドHC 吸出量 (g/test)	コールドHC 吸着量 (g/test)	未浄化 脱離HC量 (g/test)	脱離HC 浄化率 (%)	脱離HC 浄化量 (g/test)
	1	2	3					
実施例 1	TWC	触媒A	触媒E	1.22	0.915	0.706	22.8	0.209
実施例 2	TWC	触媒F	触媒E	1.22	0.915	0.705	23.0	0.210
実施例 3	TWC	触媒G	触媒E	1.22	0.915	0.704	23.1	0.211
実施例 4	TWC	触媒H	触媒E	1.22	0.915	0.702	23.3	0.213
実施例 5	TWC	触媒I	触媒E	1.22	0.915	0.703	23.2	0.212
実施例 6	TWC	触媒J	触媒E	1.22	0.915	0.700	23.5	0.215
実施例 7	TWC	触媒A	触媒K	1.22	0.927	0.708	23.6	0.219
実施例 8	TWC	触媒F	触媒L	1.22	0.939	0.719	23.4	0.220
実施例 9	TWC	触媒G	触媒M	1.22	0.903	0.683	24.4	0.220
実施例 10	TWC	触媒H	触媒N	1.22	0.939	0.718	23.5	0.221
実施例 11	TWC	触媒I	触媒O	1.22	0.952	0.731	23.2	0.221
実施例 12	TWC	触媒J	触媒E	1.22	0.915	0.695	23.9	0.219
比較例 1	TWC	触媒L	触媒E	1.22	0.915	0.714	22.0	0.201
比較例 2	TWC	触媒P	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 3	TWC	触媒Q	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 4	TWC	触媒R	触媒E	1.22	0.915	0.713	22.0	0.202
比較例 5	TWC	触媒A	触媒U	1.22	0.915	0.910	0.55	0.005
比較例 6	TWC	触媒A	触媒V	1.22	0.915	0.759	17.0	0.156
比較例 7	TWC	触媒A	触媒W	1.22	0.915	0.915	0.000	0.000

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing an example of an evaluation system which enforces the exhaust gas purification approach of this invention effectively.

[Translation done.]

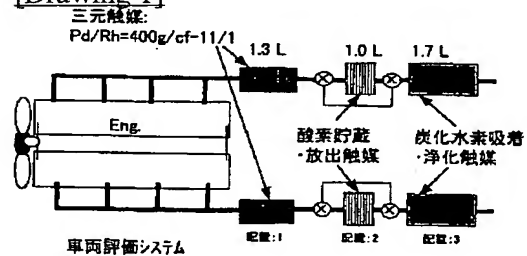
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DRAWINGS

[Drawing 1]



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